FLUORINE-CONTAINING HETEROCUMULENES

COMMUNICATION 12.* N-BENZENESULFONYLBIS(TRIFLUOROMETHYL)KETENIMINE AND ITS ADDUCTS WITH KF AND KHF_2

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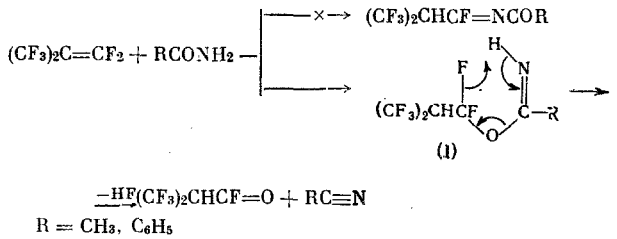
Previously it was shown that the reaction of perfluoroisobutylene (PFIB) with primary amines leads to the N-substituted imidoylfluorides of α-hydrohexafluoroisobutyric acid, the dehydrofluorination of which is a convenient method for the synthesis of either N-alkyl- or N-arylbis(trifluoromethyl)ketenimines [2]. It was postulated that N-acylbis(trifluoromethyl)ketenimines could be synthesized from PFIB and acid amides by an analogous sequence of reactions, which compounds have definite interest in connection with studying the reactivity of fluorine-containing heterocumulenes.

However, it proved that the main reaction products of PFIB and carboxylic acid amides are the nitriles of the corresponding acids and α-hydrohexafluoroisobutyryl fluoride. Neither N-acylated imidoylfluorides nor ketenimines were detected in the reaction mixture. This result is apparently due to the fact that the multiple bond in PFIB is attacked by the nucleophilic oxygen of the carboxamido group of the ambident amide. This leads to the intermediate iminoester (I), which then decomposes to give the end product. The addition product of AcOH to PFIB undergoes a similar decomposition [3].



Due to its low nucleophilicity, benzenesulfonamide does not react with PFIB. At the same time, in [4] it was established that PFIB reacts easily in CH_3CN solution with the K salt of benzenesulfonamide (II). Since the composition of the reaction products could be judged only by the results of hydrolyzing the reaction mixture,† a study of this reaction was continued by us.

It proved that the reaction of PFIB with salt (II) (reactant mole ratio = 2 : 1) gives in quantitative yield the CH_3CN-soluble adduct of N-benzenesulfonyl-bis(trifluoromethyl)ketenimine with KF (V) and $(CF_3)_3CH$. The structure of (V) was proved by its conversion to α-hydrohexafluoroisobutyric acid N-benzenesulfonimidoylfluoride (VI) by treatment with anhydrous HCl and to sulfonamide (III) by hydrolysis, and also by synthesis from KF and N-benzenesulfonylbis(trifluoromethyl)ketenimine (VII). Ketenimine (VII) could be obtained by the dehydrofluorination of imidoylfluoride (VI) using the complex $Et_3N \cdot BF_3$ (cf. [1]). As a result, it is obvious that when PFIB reacts with salt (II) the benzenesulfonamide anion adds to the

*See [1] for Communication 11.

†Two products were isolated: α-hydrohexafluoroisobutyric acid N-benzenesulfonamide (III) and trifluoromethylmalonic acid mono-N-benzenesulfonamide (IV).

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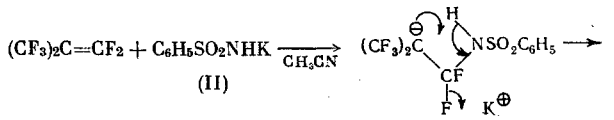
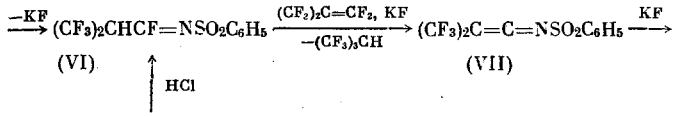
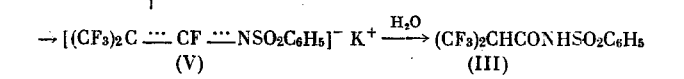
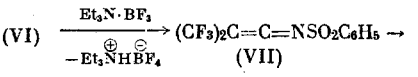
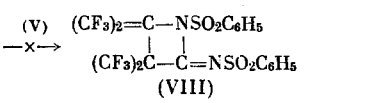
fluoroolefin, which is accompanied by the elimination of F^- from the difluoromethylene group. The thus-formed imidoylfluoride (VI) is dehydrofluorinated under the reaction conditions by the perfluoroisobutylene, which leads to ketenimine (VII) and the hydrofluorination product of PFIB, namely $(CF_3)_3CH$ ([2, 5]). In the final step of the reaction the F^- adds to ketenimine (VII) to give adduct (V).







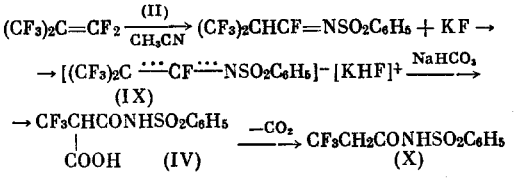




It should be mentioned that ketenimine (VII) cannot be generated from adduct (V) by heating. Compound (V) is quite stable at 20°C, but it decomposes above 100°, in which connection the main decomposition product is benzenesulfonyl fluoride. This decomposition is also characteristic for ketenimine (VII). At the same time the analogous adduct of hexafluoroacetone with KF, which is also stable under ordinary conditions, decomposes into the starting components when heated [6].

The previously studied bis(trifluoromethyl)ketenimines are apparently also capable of adding KF to give adducts of the (V) type. However, these adducts cannot be isolated, and they only play the role of intermediates during the dimerization of the ketenimines using KF [7]. Ketenimine (VII) does not form the dimer (VIII), apparently due to the low nucleophilicity of the mesomeric anion of salt (V), which is incapable of adding to ketenimine (VII).

On the basis of the above said it could be expected that when PFIB is reacted with salt (II) in the absence of excess fluoroolefin, i.e. using a 1:1 mole ratio of the reactants (under the conditions described in [4]), the reaction product will be imidoylfluoride (VI). Actually, the imidoylfluoride is not dehydrofluorinated in this case, but the KF that is formed in the reaction causes the deprotonation of imidoylfluoride (VI), which is a strong CH acid. As a result, the reaction leads to the formation of the saltlike compound (IX). This compound contains the same mesomeric carbanion that is present in (V), which follows from the complete similarity in the IR and ^{19}F NMR spectra of both salts, and also their chemical equivalence. Thus, salt (IX) when treated with anhydrous HCl is converted to the free CH acid, namely imidoylfluoride (VI), and to sulfonamide (III) by acid hydrolysis. The alkaline hydrolysis of salt (IX) leads to the saponification of one CF_3 group to the carboxyl group. The thus-formed acid (IV) is decarboxylated to give N-benzenesulfonyltrifluoropropionamide (X)



The fact that the adduct of ketenimine (VII) with which either KF or salt (IX) is obtained, which, in turn, can be regarded as the adduct of ketenimine (VII) with KHF_2, when PFIB is reacted with the K salt of benzenesulfonamide serves as quite definite evidence that this reaction represents the usual example of "vinyl" substitution in fluoroolefins. As a result, the statement made in [4] that "allylic" substitution also occurs in this reaction, which statement is based on the isolation of acid (IV), must be considered as lacking sufficient substantiation (see [8, 9] regarding allylic substitution in the reactions of PFIB with nucleophilic reagents).

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 instrument. The NMR spectra were recorded on a Perkin — Elmer R-12 instrument (60 MHz), and the chemical shifts were measured from TMS (external standard). The ^{19}F NMR spectra were recorded on a Hitachi H-6013 instrument (56.46 MHz), and the chemical shifts were measured in parts per million from CF_3COOH (external standard).

Reaction of PFIB with the K Salt of Benzenesulfonamide. a) To a suspension of 8.4 g (0.043 mole) of salt (II) in 50 ml of abs. CH_3CN, cooled to −40°, was added 20 g (0.1 mole) of PFIB. The stirred mixture was warmed up to 0° and kept at this temperature until a homogeneous solution was obtained (~1 h), after which it was heated at 20° for 1 h, the unreacted PFIB, $(CF_3)_3CH$, and CH_3CN were vacuum-distilled at 20-25°, 50 ml of abs. CH_2Cl_2 was added to the residue, and the obtained precipitate was filtered and dried in vacuo over P_2O_5. We obtained 15.5 g (95%) of adduct (V). Found: C 31.46; H 1.41; F 35.63%; $C_{10}H_5F_7NO_2SK$. Calculated: C 32.02; H 1.33; F 35.43%. Infrared spectrum (in Nujol, ν, cm^{-1}): 1610-1640. ^{19}F NMR spectrum in CH_3CN): −30.8 m (CF); −26.2 d.g. (trans-CF_3); −24.6 d.g. (cis-CF_3); $J_{CF_3-CF_3}$ = 9.6; $J_{cis\text{-}CF_3-F}$ = 27.4, $J_{trans\text{-}CF_3-F}$ = 13 Hz. NMR spectrum (in CH_3CN): 7.35 (center of multiplet (C_6H_5).

b) With stirring and cooling in ice, a suspension of 9.7 g (0.05 mole) of salt (II) in 25 ml of abs. CH_3CN was added to 10 g (0.05 mole) of PFIB in 25 ml of abs. CH_3CN. When the precipitate had dissolved the mixture was heated up to 20-22°, the CH_3CN was then evaporated in vacuo, and CH_2Cl_2 was added to the residue. The precipitate contained 14.8 g (75%) of adduct (IX). Infrared spectrum (in Nujol, ν, cm^{-1}): 1610-1640. ^{19}F NMR spectrum (in CH_3CN): −30.5 q.q. (CF); −26.6 d.q. (trans-CF_3), −24.5 d.q. (cis-CF_3); $J_{CF_3-CF_3}$ = 9.6, $J_{cis\text{-}CF_3-F}$ = 26.6, $J_{trans\text{-}CF_3-F}$ = 14.5 Hz.

α-Hydrohexafluoroisobutyric Acid N-benzenesulfonimidoylfluoride (VI). With stirring, dry HCl was passed into a suspension of 11 g of adduct (V) in 50 ml of abs. CH_2Cl_2 until saturated. The precipitate was filtered. From the filtrate by distillation we isolated 9 g (90%) of imidoylfluoride (VI), bp 114-116° (6 mm), 87-89° ($8\cdot10^{-3}$ mm). Found: C 35.55; H 1.78; F 39.33%. $C_{10}H_6F_7NO_2S$. Calculated: C 35.61; H 1.80; F 39.45%. Infrared spectrum (ν, cm^{-1}): 1710 (C=N). NMR spectrum (in CH_3CN): 5.0 d.h. (CH); 7.8 m (C_6H_5); J_{CH-CF} = 10.5, J_{CH-CF_3} = 7.7 Hz. ^{19}F NMR spectrum (in CH_3CN): −84 m (CF); −15.4 t (CF_3); $J_{CF_3-F} = J_{CF_3-H}$ = 8 Hz.

N-Benzenesulfonylbis(trifluoromethyl)ketenimine (VII). To a solution of 2.5 g of the $Et_3N\cdot BF_3$ complex in 5 ml of abs. ether was added 5 g of imidoylfluoride (VI) in 5 ml of abs. ether. The mixture was kept at 20° for 4 h and the precipitate was filtered. Distillation of the filtrate gave 1.6 g (35%) of ketenimine (VII), bp 58-60° ($7\cdot10^{-3}$ mm). Found: C 37.85; H 1.61; F 35.52; N 4.42%. $C_{10}H_5F_6NO_2S$. Calculated: C 37.83; H 1.58; F 35.96; N 4.44%. Infrared spectrum (ν, cm^{-1}): 2055 (C=C=N). ^{19}F NMR spectrum (in ether): −22.1 s.

Ketenimine (VII) (2.8 g) was slowly heated up to 250°. We obtained a mixture of products, the distillation of which gave 1 g (70%) of benzenesulfonyl fluoride, bp 77-78° (7 mm). ^{19}F NMR spectrum (in ether): −147 s. In a similar manner, from 1.5 g of adduct (V) by heating up to 250° in vacuo (0.008 mm) we obtained 0.4 g (62%) of benzenesulfonyl fluoride. A suspension of 0.36 g of KF, 2 g of ketenimine (VII), and 10 ml of abs. CH_3CN was stirred at 20° until a homogeneous solution was obtained. The CH_3CN was removed in vacuo, and the solid residue was washed with CH_2Cl_2, and then with ether. We obtained 1.5 g (63%) of adduct (V), which was identical (NMR) with that described above.

Chlorination of Adduct (IX). With shaking, 3 g of chlorine was passed into a suspension of 3 g of (IX) in abs. CH_2Cl_2, the precipitate was filtered, and the CH_2Cl_2 was distilled from the filtrate. The residue was $(CF_3)_2CClCF=NSO_2C_6H_5$ (XI) as an oil. ^{19}F NMR spectrum (in CCl_4): −74 h (CF); −9 d (CF_3); J = 9.5 Hz. The crude (XI) was dissolved in aqueous acetone, and when exothermic reaction had ceased the mixture was poured into water. Extraction with ether gave 2.3 g of $(CF_3)_2CCl-CONHSO_2C_6H_5$, mp 83-85° (from hexane). Found: C 32.48; H 1.68; F 31.42%. $C_{10}H_6ClF_6NO_3S$. Calculated: C 32.52; H 1.62; F 30.93%. Infrared spectrum (ν, cm^{-1}): 1735 (C=O), 3230-3280 (HB). ^{19}F NMR spectrum (in CCl_4): −10 s.

Hydrolysis of Adducts (V) and (IX). A mixture of 3.1 g of adduct (IX) and 10% HCl solution was heated up to 100°. The mixture after cooling was extracted with ether to give 2.45 g (92%) of sulfonamide (III), mp 154-157° (from $CHCl_3$) [4]. NMR spectrum (in CH_3CN): 3.8 h (CH); 5.25 br. s. (NH); 7-7.75 m (C_6H_5). ^{19}F NMR spectrum: −14.5 d; J = 8 Hz.

A solution of 2.2 g of adduct (V) in water was acidified. The precipitate contained 1.8 g (90%) of sulfonamide (III).

With shaking, 4.2 g of adduct (IX) was dissolved in saturated $NaHCO_3$ solution. After 20 h the solution was acidified. Extraction with ether gave 1.7 g (54%) of sulfonamide (X), which was identical (NMR) with that described in [4].

Reaction of PFIB with Acetamide. With stirring and cooling, 18 g of PFIB was passed in 2 h into a solution of 2.5 g of acetamide in 30 ml of abs. diglyme. The stirring was continued for 3 h at 20°. Then, with heating up to 100°, a mixture of $(CF_3)_3CH$, $(CH_3)_2CHCOF$, and CH_3CN (GLC) was distilled into a trap (−78°) in a vacuum of 70 mm. Distillation over conc. H_2SO_4 gave 6 g (71%) of $(CF_3)_2CHCOF$, which was identified via the ^{19}F NMR spectrum and by conversion to $(CF_3)_2CHCOOC_2H_5$ by treatment with alcohol.

CONCLUSIONS

1. The adducts of N-benzenesulfonylbis(trifluoromethyl)ketenimine with either KF or KHF_2 are formed when perfluoroisobutylene is reacted with the K salt of benzenesulfonamide.

2. N-Benzenesulfonylbis(trifluoromethyl)ketenimine was synthesized and some of its properties were studied.

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